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Efficiency of Gas-Wall Reactions in a Cylindrical Flow Reactor

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SECTION I

INTRODUCTION

In a recent study (1), we attempted to establish the efficiency of NO_2-wall reactions in a cylindrical flow reactor. In particular, we tried to measure the reaction efficiency ϕ, defined as the fraction of NO_2-wall collisions that leads to the removal of NO_2 from the gas phase (via adsorption or reaction). The general case of gas-wall reactions has been treated previously by Paneth and Herzfeld (2) and Wise and Ablow (3) for $\phi \ll 1$ and $\phi \ll 1$. (Related solutions have also been given by Jost (4) and Carslaw and Jaeger (5)). The intermediate case (ϕ comparable to unity but not necessarily equal to unity), which was of interest in our work, was not treated by these authors.

In this report, we derive a general solution applicable for all values of ϕ. This solution becomes identical to the published results for the limiting cases of $\phi \ll 1$ and $\phi \ll 1$. In addition, we perform a one-dimensional random walk analysis of gas-wall reactions, which, in conjunction with the diffusion equation solution, gives a clear physical picture of the collision-reaction process. These solutions are applied to our specific case of interest (NO_2-wall reactions) as an example.

The utility of these solutions, however, is wide spread. They can be used to obtain wall reaction rate constants for many reactions since the information content of fitting experimental results to diffusion-limited kinetic expressions is limited. In many cases, such as heterogeneous catalysis and surface-initiated reactions, the specific information desired is lost in attempts to analyse experimental results in terms of limiting cases of wall collision efficiencies.

SECTION 4

GENERAL SOLUTION FOR FLOW, DIFFUSION AND WALL REACTIONS IN A CYLINDRICAL REACTOR

We consider a system in which the cylindrical walls (but not the ends) of a tubular flow reactor are coated with catalyst. We assume that C, the reacting gas, disappears via a heterogeneous first-order process (adsorption or reaction) that occurs on the walls with an efficiency ϕ. If the reacting gas is introduced into the system as a dilute component in a large concentration of inert gas, we can assume that the total pressure P and therefore D, the diffusion coefficient of C in the mixture, are approximately constant during the course of reaction. Fick's second law of diffusion with an additional term for flow in the direction of the cylinder axis (under steady-state conditions) is (2-4)

$$D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2}\right) - v_0 \frac{\partial C}{\partial z} = 0 \qquad (1)$$

where r = radial cylindrical coordinate

z = longitudinal cylindrical coordinate

v_0 = the linear flow rate in the z direction (equal to F/A, the volume flow rate divided by the cross-sectional area of the cylinder)

The following boundary conditions are applicable to the solution of Eq. 1 for the case of interest here

$$C\ (r,\ z=0) = C_0$$

$$\frac{\partial C}{\partial r}\ (r=0,\ z) = 0 \qquad (2)$$

$$D\frac{\partial C}{\partial r}\ (r=R,\ z) = \phi\, k_g C'$$

where C_0 = the initial concentration of C

R = the cylinder radius

k_r = the average velocity of the reacting molecule in the radial direction

$[k_r = (kT/2\pi m)^{\frac{1}{2}}$

where k = the Boltzmann constant

T = the absolute temperature

m = the mass of the reacting gase molecule (6)]

C' = the concentration of C one mean free path away from the wall

The last boundary condition in Eq. 2 arises from our assumption that a fraction of reactant molecules ϕ is removed from the gas phase on collision with the walls via adsorption or reaction. Alternatively, we might consider a reaction scheme involving simple first-order adsorption, desorption, and reaction. Then the last boundary condition in Eq. 2 would be replaced by

$$D\frac{\partial C}{\partial r} = k_a C' - k_d C_a = \gamma (1 - f) k_r C' - k_d C_a$$

where k_a = the rate constant for adsorption

k_d = the rate constand for desorption

C_a = the concentration of adsorbed C

γ = the sticking coefficient

f = the fractional surface coverage

If we assume a steady state for C_a, we may write

$$\frac{dC_a}{dt} = \gamma(1 - f)k_r C' - k_d C_a - k_s C_a = 0$$

where $k_s C_a$ = the rate of surface reaction of adsorbed C.

Solving the latter equation for C_a and substituting the result into the former equation we find

$$D\frac{\partial C}{\partial r} = \gamma(1 - f)\left(\frac{k_a}{k_d + k_s}\right) k_r C'$$

Comparison of this expression with the last boundary condition in Eq. 2 indicates that for the case discussed here,

$$\phi = \gamma(1 - f)\left(\frac{k_a}{k_d + k_a}\right).$$

Fanesh and Herzfeld (2) and later Wise and Ablow (3) assumed $C(R) \cong C'$ and obtained the solution of Eq. 1 on the basis of the boundary conditions in Eqs. 2. This assumption, however, is valid only for $\phi << 1$. In general, $C(R) = (1 - \phi)C'$. If we apply this assumption and the boundary conditions in Eqs. 2, the solution of Eq. 1, following the methods described by other workers (2-5), is

$$\frac{C}{C_0} = \sum_{i=1}^{\infty} \frac{2J_0(\rho_i \frac{r}{R})}{\rho_i\left(1 + \delta^2 \rho_i^2\right)J_1(\rho_i)} \exp(\alpha_i z) \tag{3}$$

where

$$\delta = \frac{D}{k_a R}\,\frac{(1 - \phi)}{\phi} \tag{4}$$

J_0 and J_1 are Bessel functions of the first kind, ρ_i is the ith root of the equation

$$J_0(\rho_i) = \delta \rho_i J_1(\rho_i) \tag{5}$$

and

$$\alpha_i = \frac{F}{2D} - \left[\left(\frac{F}{2D}\right)^2 + \left(\frac{\rho_i}{R}\right)^2\right]^{1/2}. \tag{6}$$

The application of the limiting cases for $\phi << 1$ or $\phi = 1$ to Eq. 3 gives the results previously reported (2-4). (Alternatively, the application of these conditions to the boundary conditions in Eqs. 2 gives the same boundary conditions specified by the previous authors for $<< 1$ or $\phi = 1$.)

F and D are related by (7)

$$D = \frac{1000\,kT}{8\pi d^2 P}\left(\frac{8kT}{\pi\mu}\right)^{1/2} \tag{7}$$

where μ is the reduced mass of the reacting and inert gas molecules, and $d = (d_m + d_n)/2$, where d_m and d_n are the molecular diameters of the reacting and inert gas molecules treated as hard spheres.

As an example, let us apply Eq.3 to the case of our experiments with NO_2-wall reactions in a cylindrical flow reactor. Nitrogen was used as the inert carrier gas with conditions such that $P_{N_2}/P_{NO_2} \approx 500$. This fulfilled the requirement that P and therefore D be approximately constant. The hard sphere diameters of NO_2 and N_2 at 298°K, which is the usual temperature for our experiments, are 0.446 and 0.371 nm, respectively (6). With these values and typical values for R, P, and F, we calculated the concentration distribution of C from Eq.3 for selected values of ϕ. Some calculated concentration profiles are shown in Figure 1. We also plotted C/C_0 as a function of z at a given value of r. This is shown in Figure 2 for r = 0 and the same parameters as in Figure 1 as well as additional values of ϕ.

In our NO_2 experiments, we determined the average value of the NO_2 concentration at r = 0 by measuring the decrease in intensity (due to optical absorption by NO_2 at 475 nm) of a narrow beam of light passing through the center of the cylinder (8). Calculated values corresponding to the average NO_2 concentration at r = 0 may be obtained by integrating the curves in Figure 2 over the length of the cylindrical reactor, or by setting r = 0 in Eq.3 and integrating. In the latter case,

$$\left(\frac{C}{C_0}\right)_{r=0} = \frac{\int_0^{\ell} \left(\frac{C}{C_0}\right)_{r=0} dz}{\int_0^{\ell} dz} = \sum_{i=1}^{\infty} \frac{2J_0(\alpha_i \frac{r}{R}) \exp(\alpha_i \ell) - 1}{\alpha_i \ell \alpha_i (1 + \phi^2 \alpha_i^2) J_1(\alpha_i)} \qquad (8)$$

where ℓ is the length of the cylinder (= 40 cm in our experiments).

In Table I $\langle C/C_0 \rangle_{r=0}$ is calculated for selected values of T, R, P, and ℓ versus P and ϕ. Note that for large values of ϕ, $\langle C/C_0 \rangle_{r=0}$ approaches a constant value because the reaction becomes diffusion-limited under such conditions. (Note also that the limiting value of $C/C_0)_{r=0}$ becomes independent of pressure below $\sim$10 torr [1] because at a very low pressure,

[1] To convert from torr to newton/meter^2, multiply by 1.333 22 E+02.

0 = F, and the limiting value of $\langle D/D_0 \rangle_{\phi=0}$ depends only on R/L, or R only for cylinders sufficiently long that $D(L)=D_0$. Conversely, for low values of ϕ, $D/D_{0\ \phi=0}$ approaches unity. Significant variations in $\langle D/D_0 \rangle_{\phi=0}$ occur only for intermediate values of ϕ; the exact range is dependent on the total pressure. Of course these variations would also be observed for $\langle D/D_0 \rangle_{r=0}$ and for D/D_0 (averaged over r) as a function of R.

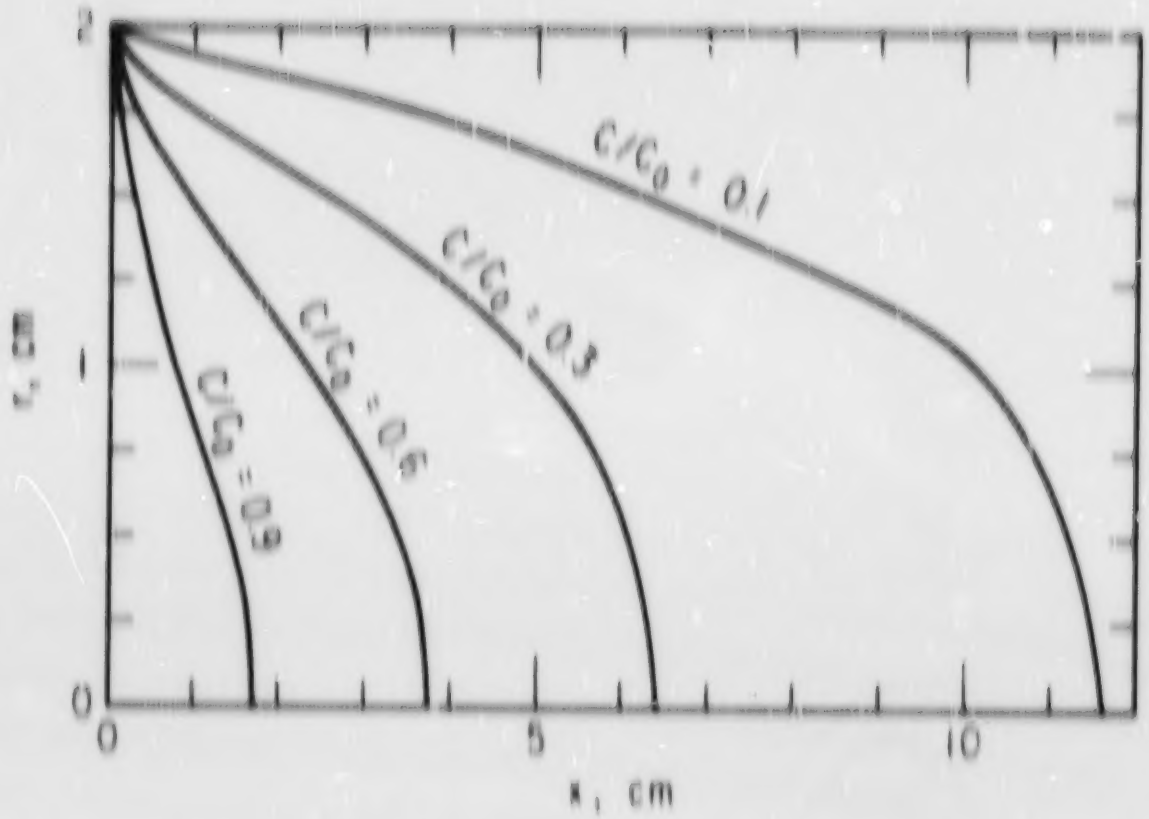

Figure 1. Concentration Contours Calculated from eq. 3 for Selected Experimental Parameters and $\phi = 1$, $P = 700$ torr ($D = 0.15$ cm^2/sec), $T = 298°K$ ($k_r = 9.3 \times 10^3$ cm/sec), $R = 2$ cm, and $F = 10$ cm^3/sec.

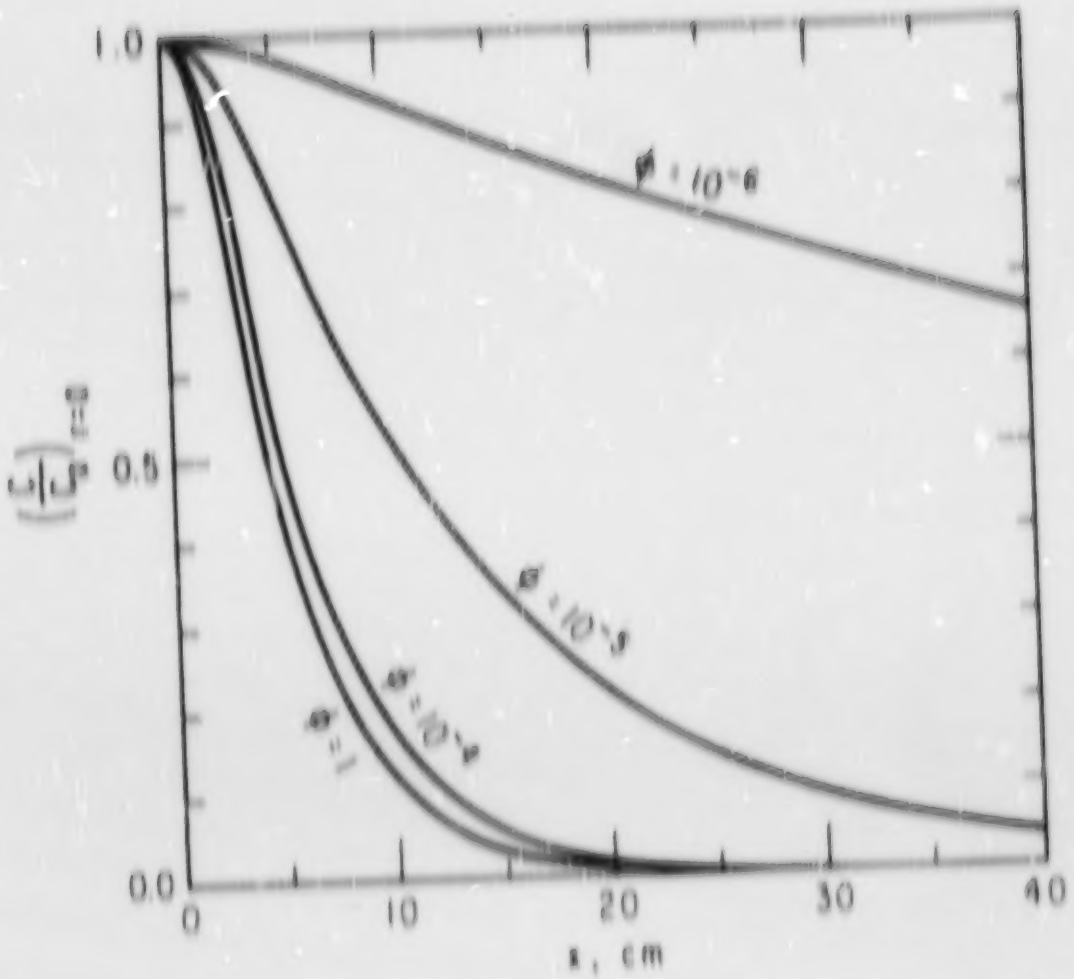

Figure 3. C/C_0 at $t = 0$ Calculated from Eq. 3 for Selected Values of β, ξ, R, and P and Various Values of ϕ. P = torr (D = 0.15 cm^2/sec), T = 298°K (k_y = 9.1 x 10^3 cm/sec), R = 2 cm, and P = 10 cm^3/sec.

TABLE 1: C/C_0 $_{r=0}$ vs P and ϕ^a

P, torr	$\left(\frac{C}{C_0}\right)_{r=0}$ for ϕ = 1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
760	0.138	0.138	0.138	0.140	0.159	0.341	0.828
100	0.038	0.038	0.038	0.041	0.064	0.259	0.806
10	0.028	0.028	0.029	0.040	0.101	0.366	0.821
1	0.027	0.028	0.038	0.090	0.271	0.620	0.883
0.1	0.027	0.038	0.089	0.266	0.589	0.839	0.949
0.01	0.027	0.085	0.260	0.586	0.834	0.944	0.982
0.001	0.027	0.249	0.584	0.834	0.943	0.982	0.994

[a]Calculated from Eq. 8 assuming the values given in Figure 1 for P, T, R, and F, and ℓ = 40 cm.

SECTION 3

RANDOM WALK ANALYSIS OF GAS-WALL REACTIONS

We consider a one-dimensional problem in which a molecule can move toward or away from a wall in equal steps and with equal probability (except at the wall, where the probability of reflection is unity). We assume that the molecule starts at a distance of $R = r_0$ cm, or n_0 steps away from the wall ($n_0 \geq 0$), and takes n steps. Gnedenko (9) has calculated the probability that the molecule will end up at a distance $R = r_f$ cm, or n_f steps from the wall, after taking n steps. This probability is equal to the sum of two probabilities; the probability of the molecule arriving at $R = r_f$ after n steps, plus the probability of the molecule arriving at $R + r_f$ if there were no reflecting barrier at R. Here, however, we desire to calculate the probability ($p\delta$) that a molecule starting at $R = r_0$ cm, or n_0 steps from the wall, will collide with the wall δ times during the n steps.

We obtain the following solution by induction

$$p\delta = \frac{1}{2^{(n-\delta)}} \quad \frac{L_i!}{\frac{1}{2}(L_i + M_i)!\ \frac{1}{2}(L_i - M_i)!} \tag{9}$$

The forms of δ, L_i, and M_i depend on the values of n_0, δ, and $n + n_0$. The various solutions are tabulated in Table 2. Two points should be made regarding the use of Eq. 9. For given values of n and n_0, there is a maximum number of collisions (δ_{max}) that can occur with the wall. The value of δ_{max} can be calculated from

$$\delta_{max} = \frac{1}{2}(n - n_0) + \frac{1}{2}\left[3 + (-1)^{(n-n_0)}\right] + \Delta \tag{10}$$

where $\Delta = 0$ for $n_0 > 0$, and $\Delta = -1$ for $n_0 = 0$. In addition, the use of Eq. 9 is subject to the condition that $p\delta = 0$ if $M_i > L_i$. Otherwise the equation is

generally applicable. For most cases of interest, $t_i \gg t_{i-1}$. Thus, Stirling's formula (9) can be used to evaluate the factorials.

TABLE 2. SOLUTIONS TO RANDOM WALK PROBLEM

$n + n_0$	n_0	β^a	$\bar{n}$	$\bar{s}_1$	$\bar{m}_1$
odd	0	01	$\beta + 1$	$n - \beta - 1$	β
odd	$\begin{cases} 0 \text{ and } 1 \\ \text{or} \\ \infty \text{ and } 01 \end{cases}$		β	$n - \beta$	$n_0 + \beta - 1$
even	0	01	β	$n - \beta$	β
even	$\begin{cases} 0 \text{ and } 1 \\ \text{or} \\ \infty \text{ and } 01 \end{cases}$		$\beta - 1$	$n - \beta + 1$	$n_0 + \beta - 1$

[a] Except for a few cases in $n_0 = 0$ or 1, the probability that a molecule will not collide with the wall, can only be calculated from $p_0 = 1 - \sum_{\beta=1}^{\beta_{max}} p_\beta$, where β_{max} is the maximum number of collisions possible for a given n and n_0.

We now apply this analysis to the example in Figure 2. We assume that the time required for the molecule to take one step is $\tau = \lambda/k_s$, where λ is the mean free path, and k_s is the average velocity in space. By using the expressions for $k_s (= 4 k_y)$ and the mean free path of one gas in a two-component mixture, we obtain $\tau = 1.6 \times 10^{-10}$ sec for the example given in Figure 2. We also assume that the length of the step (in the radial direction) is equal to $\lambda \times k_y$ divided by the average velocity in space, or $1/4\lambda$. The latter value is equal to 1.3×10^{-6} cm for the example given in Figure 2. In addition, $n_0 = 2/(1.3 \times 10^{-6}) = 1.54 \times 10^6$ for a molecule starting at the center of the cylinder. In Figure 2, the linear velocity v_0 down the cylinder is 0.80 cm/sec. Thus, in the 1.25 sec required for the molecule to traverse 1 cm in the x direction, it will take $1.25/\tau = 1.25 \times 10^{10}$ random steps (except at the wall) of 1.3×10^{-6} cm length in the radial direction.

Results of calculations for $t = 1.25$ sec ($n = 1.25 \times 10^{10}$) versus $\beta = r_0$ or n_0 and β are given in Table 3. Only 11% of the molecules will collide with the wall during this interval[2], and those that do collide with the wall do so many times ($10^5 < \beta < 10^5$). Results of calculations for the same example integrated over r for various values of t or x are given in Table 4. Here again, those molecules that collide with the wall do so many times. Of course, the total fraction of molecules that collide with the wall decreases as t and x decrease. In addition, the peak in the distribution of molecules that collide with the wall shifts to lower values of β as t and x decrease.

[2]The total number of gas-wall collisions for this case is $\sim 2.2 \times 10^{24}$ sec^{-1} compared with 2.4×10^{24} sec^{-1} calculated from simple kinetic theory(5).

TABLE 3. MOLECULE - WALL COLLISIONS VS Y_0[a]

$R = r_0$, cm	Fraction of Molecules in Interval	n_0	$\beta = 0$	Fraction of Molecules in Interval With $1 \times 10^{-6} < \beta < 10^{-5}$	$10^{-5} < \beta < 10^{-4}$	$10^{-4} < \beta < 10^{-3}$	$10^{-3} < \beta < 10^{-2}$	$10^{-2} < \beta < 10^{-1}$	$\beta = 10^{0}$
1.98 - 2.00	0.05	1.94×10^{4}	0.129	0.000	0.000	0.003	0.024	0.095	0.091
1.95 - 1.98	0.05	5.89×10^{4}	0.401	0.000	0.000	0.004	0.054	0.181	0.159
1.84 - 1.90	0.05	9.93×10^{4}	0.685	0.000	0.000	0.005	0.041	0.165	0.077
1.79 - 1.84	0.05	1.31×10^{5}	0.791	0.000	0.000	0.001	0.020	0.104	0.216
1.61 - 1.79	0.10	2.06×10^{5}	0.929	0.000	0.000	0.001	0.011	0.008	0.007
<1.61	0.10	$<5.06 \times 10^{5}$	<0.987	0.000	0.000	0.000	<0.004	<0.000	<0.001
0:0	1.00		0.490	0.000	0.000	0.001	0.011	0.070	0.000

[a]Calculated for the example in Figure 2 with $t = 1.35$ sec, the time required for the average molecule to traverse 1 cm in the x direction.

TABLE 4: MOLECULE - WALL COLLISIONS VS t OR s[a]

t[b], sec	s, cm	Fraction of Molecules With n = 0	$1 \leq n \leq 10$	$10 \leq n \leq 10^2$	$10^2 \leq n \leq 10^3$	$10^3 \leq n \leq 10^4$	$10^4 \leq n \leq 10^5$	$10^5 \leq n \leq 10^6$
0.0145	0.01	0.959	0.000	0.000	0.001	0.008	0.008	0.000
0.145	0.1	0.864	0.000	0.000	0.001	0.010	0.085	0.000
1.45	1.0	0.890	0.000	0.000	0.001	0.011	0.078	0.020
3.75	3.0	0.815	0.000	0.000	0.000	0.011	0.082	0.091
7.50	6.0	0.749	0.000	0.000	0.000	0.010	0.083	0.156
15.5	10.0	0.688	0.000	0.000	0.000	0.010	0.084	0.218

[a] Calculated for the example in Figure 4 with t = 1.45 sec, the time required for the average molecule to traverse 1 cm in the s direction.

SECTION 5

DISCUSSION

The results obtained from the solution of the differential equation for diffusion and flow in a cylindrical reactor indicate that only intermediate values of ϕ ($\approx 10^{-4}$-10^{-6}) could be determined for the example cited. For smaller values of ϕ, the reaction would be too slow. For higher values, the reaction becomes diffusion-limited and independent of ϕ.

Examination of the behavior of individual molecules via the random walk analysis shows that, for the example cited, those molecules that collide with the wall do so many times within a short interval of time, or n. The peak in the distribution of molecules that collide with the wall (for all but very small values of t and n) lies at $\theta \approx 1 \times 10^{5}$. This is about what would be expected in an experiment where the limiting sensitivity for ϕ is $\sim 10^{-4}$.

We have investigated these results further to determine the conditions under which higher or lower values of ϕ could be resolved experimentally. It was found that by increasing the cylinder length or decreasing the flow rate or cylinder radius, alone or in combination, the sensitivity for lower values of ϕ could be increased. The reverse would be true for higher values of ϕ. Decreasing the pressure would also give a greater distinction of high values of ϕ. However, at very low pressures, few gas-wall collisions would occur, and the flow rate would have to be decreased or the reactor length increased in conjunction with the pressure decrease.

We have also examined the possibility of obtaining greater definition by running the analyzing light beam near the wall, rather than down the center of the cylinder, or perpendicular to the cylinder axis. Although greater definition would be obtained in this manner, experimental difficulties would be greater and, depending on the particular experimental conditions, extremely accurate measurements of distances would be required.

Although our discussion of the experimental variation of the sensitive range of ϕ is based on a particular example, the conclusions are generally applicable. Thus, we conclude that making appropriate changes in flow rates or pressure is the easiest and most accurate method for establishing the experimental sensitivity range for ϕ. Experimental sensitivities for detecting changes in reactant concentration will probably be limiting, as will very high flow rates or pressures. In the latter cases, drag at the walls may become significant, and the condition implicit in Eq. 1 that v_0 is independent of r (and z) may no longer be valid. Changes in the dimensions of the reactor will affect the sensitivity range. However, practical limits for variation of these parameters are generally more severe than those for flow and particularly pressure. The examination of changes in reactant concentration near $r = R$ provides an alternative method for varying the sensitivity range for ϕ. The general limits in this case concern the accuracy and the resolution at which distances from the wall can be measure.

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